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(54) INK-JET RECORDING INK, INK-JET RECORDING INK SET, RECORDING METHOD, PRINT, AND INK-JET RECORDING APPARATUS

(57) Provided are an ink jet recording ink (IJ ink), an ink jet recording ink set (IJ ink set) and a recording method, having excellent dispersion stability and ejection stability and being capable of providing images which is free from bleeding and which is excellent in color development property and rubbing resistance. An IJ ink and an IJ ink set having long-term storage stability are provided. Also provided are recorded matter having excellent color development property and rubbing resistance, and an ink jet recording apparatus capable of providing the same.

The invention includes: an IJ ink containing a colorant of a pigment and/or dye enveloped in a polymer, and water, and containing at least one compound selected from the group consisting of acetylene glycol surfactants, acetylene alcohol surfactants, glycol ethers and 1,2-alkylene glycols; an IJ ink set comprising a plurality of the inks; a recording method of using the ink and/or the ink set; recorded matter printed according to the recording method; and an ink jet recording apparatus having an electrostrictive unit mounted thereon and is designed so as to be capable of ejecting the ink.

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the present invention, examples thereof include, for example, oil-soluble dyes, basic dyes, disperse dyes, vat dyes, sulfide dyes, organic solvent-soluble dyes, and reactive dyes.

[0061] The pigment for use in the invention is not particularly limited, and any of inorganic dyes and organic dyes can be used. The inorganic dyes include, for example, metallic dyes such as copper oxides, iron oxides, and titanium oxides; and carbon blacks such as furnace black, lamp black, acetylene black, and channel black. The organic pigments include, for example, azo pigments (including azo lakes, insoluble azo pigments, condensed azo pigments, chelate azo pigments), polycyclic pigments (e.g., phthalocyanine pigments, perylene pigments, perinone pigments, anthraquinone pigments, quinacridone pigments, dioxane pigments, thioindigo pigments, isoindolinone pigments, quinofuranone pigments), dye chelates (e.g., basic dye chelates, acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

[0062] As the pigment for black ink, C.I. Pigment Black 11 which is an iron oxide; C.I. Pigment Black 7 which is a carbon black; and C.I. Pigment Black 1 which is an aniline black can be mentioned. More specifically, the following carbon blacks can be exemplified: Mitsubishi Chemical's No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100, No. 2200B; Columbia's Raven 5750, Raven 5250, Raven 5000, Raven 3500, Raven 1255, Raven 700; Cabot's Regal 400$, Regal 330R, Regal 660R, Mogul L, Monarch 700, Monarch 800, Monarch 880, Monarch 900, Monarch 1000, Monarch 1100, Monarch 1300, Monarch 1400; Dexxa's Color Black FW1, Color Black Fw2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, Printex 35, Printex U, Printex V, Printex 140U, Special Black 6, Special Black 5, Special Black 4A, Special Black 4.

[0063] Examples of the pigment for yellow ink include C.I. Pigment Yellow 1 (Fast Yellow G), 2, 3, 12 (Disazo Yellow AAA), 13, 14, 16, 17, 24, 34, 35, 37, 42 (yellow iron oxide), 53, 55, 73, 74, 75, 81, 83 (Disazo Yellow HR), 93, 95, 97, 98, 100, 101, 104, 108, 109, 110, 114, 117, 120, 128, 129, 138, 151, 153 and 154.

[0064] Examples of the pigment for magenta ink include C.I. Pigment Red 1, 2, 3, 5, 7. 12, 17, 22 (Brilliant Fast Scarlet Red), 23, 31, 38, 48 (Ca), 48 (Mn), 48:2 (Permanent Red 2B (Ba)), 48:2 (Permanent Red 2B (Ca)), 48:3 (Permanent Red 2B (Sr)), 48:3 (Permanent Red 2B (Mn)); 49:1, 52:2, 53:1, 57)Ca), 57:1 (Brilliant Carmine 6B), 60:1, 63:1, 63:2, 64:1, 81 (Rhodamine 6G Lake), 83, 88, 101 (red iron oxide), 104, 105, 106, 108 (cadmium red), 112, 114, 122 (quinacridone magenta), 123, 146, 149, 166, 168, 170, 172, 177, 178, 179, 184, 185, 190, 193, 202, 209 and 219.

[0065] Examples of the pigment for cyan ink include C.I. Pigment Blue 1, 2, 3, 15 (Phthalocyanine Blue R), 15:1, 15:2, 15:3 (Phthalocyanine Blue G), 15:4, 15:6 (Phthalocyanine Blue E), 15:34, 16, 17:1, 22, 56, 60 and 63, C.I. Vat Blue 4, and C.I. Vat Blue 60.

[0066] Examples of the pigment for green ink include C.I. Pigment Green 1, 4, 7, 8, 10, 17, 18 and 36.

[0067] With regard to the particle size of the pigment, pigments comprising particles of at most 0.5 μm are preferred, and pigments comprising particles falling between 0.01 and 0.15 μm are more preferred.

[0068] The addition amount of the colorant of such pigment and/or dye enveloped in a polymer preferably falls between 0.5 % by weight and 30 % by weight, more preferably between 1.0 % by weight and 12 % by weight. If the addition amount is smaller than 0.5 % by weight, printed density tends to become hardly ensued. On the other hand, if larger than 30 % by weight, there is a tendency that a viscosity increase of the ink or a structural viscosity in the viscosity characteristics is caused to thereby deteriorate the ejection stability.

[0069] In the colorant of the pigment and/or dye enveloped in a polymer, the content of the polymer is preferably at least 10 % by weight, more preferably at least 20 % by weight, still more preferably at least 30 % by weight with respect to the whole amount of the colorant. When the polymer content is not smaller than 10 % by weight, in particular, the property of recovering from nozzle clogging becomes good. In case of color inks (e.g., cyan ink, magenta ink, yellow ink, etc.), the color transparency through transparent sheets such as OHP sheet becomes further good.

[0070] When the polymer content in the colorant is smaller than 10 % by weight, the above-mentioned acetylene alcohol surfactants, acetylene glycol surfactants, glycol ethers, polyalcohols and substances of formula (2) may partially swell the polymer. In such a case, the polymer readily peels off from the pigment, sometime resulting in an increase viscosity of the ink.

[0071] The colorant of the pigment and/or dye enveloped in a polymer is described in more detail below. The term "enveloping" as used in the present invention means that the pigment and/or dye for the colorant is completely enveloped in a polymer.

[0072] The polymer that envelops the pigment and/or dye therein preferably comprises, as a main component, at least one member selected from the group consisting of vinyl polymers such as polyacrylates, styrene-acrylic acid copolymers, polystyrenes; and polyesters, polyamides, polyimides, silicon-containing polymers and sulfur-containing polymers.

[0073] If an ordinary pigment (not enveloped in a polymer) is dispersed in water by a dispersant, and a compound selected from acetylene glycol surfactants, acetylene alcohol surfactants, glycol ethers and 1,2-alkylene glycols is added to the aqueous dispersion, then the dispersant readily drops off from the pigment surface, and the compound may adhere to the pigment in place of the dropped dispersant. As a result, a phenomenon that the dispersant having dropped off from the pigment disturbs the printing readily occurs. In contrast, where the above-described polymer is

used for enveloping the pigment and/or dye therein, the polymer can stably envelop the colorant therein, making it difficult to cause the phenomenon mentioned above. Therefore, the use of the colorant of the pigment and/or dye enveloped in the polymer as a colorant of an ink composition makes it possible to attain stable ejection and satisfactory images.

[0074] In one particularly preferred embodiment of the invention, suitable examples of the polymer include those prepared by polymerizable monomers or oligomers having a double bond of an acryloyl, methacryloyl, vinyl or allyl group through ordinary polymerization using a polymerization initiator.

[0075] The monomers include, for example, styrene, tetrahydrofurfuryl acrylate, butyl methacrylate, (α, 2, 3 or 4)-alkylstyrenes, (α, 2, 3 or 4)-alkoxystyrenes, 3,4-dimethylstyrene, α-phenylstyrene, divinylbenzene, vinylnaphthalene, dimethylamino (meth)acrylate, dimethylaminoethyl (meth)acrylate, dimethylaminopropylacrylamide, N,N-dimethylaminoethyl acrylate, acryloylmorpholine, N,N-dimethylacrylamide, N-isopropylacrylamide, N,N-diethylacrylamide, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, ethylhexyl (meth)acrylate, other alkyl (meth)acrylates, methoxydiethylene glycol (meth)acrylate, ethoxy, propoxy or butoxy-having diethylene glycol or polyethylene glycol (meth)acrylates, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acrylate, isobornyl (meth)acrylate, hydroxyalkyl (meth)acrylates, fluorine, chlorine or bromine-containing (meth)acrylates, (meth)acrylamides, maleic acid amides; and for additionally introducing a crosslinked structure to monofunctional (meth)acrylic acids, examples thereof include acryl or methacryl group-having compounds such as (mono, di, tri, tetra, poly)ethylene glycol di(meth)acrylates, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol (meth)acrylates, trimethylolpropane tri(meth)acrylate, glycerin (di, tri)(meth)acrylates, bisphenol A or bisphenol F-ethylene oxide adduct di(meth)acrylates, neopentyl glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate and dipentaerythritol hexa(meth)acrylate.

[0076] The polymerization initiator may be any ordinary one generally used in radical polymerization, including, for example, potassium persulfate, ammonium persulfate, as well as hydrogen persulfate, azobisisobutyronitrile, benzoyl peroxide, dibutyl peroxide, peracetic acid, cumemehydroperoxide, t-butylhydroxyperoxide, paramenthanehydroxyperoxide. However, preferred for use herein are water-soluble polymerization initiators.

[0077] Examples of the method for enveloping the pigment and/or dye in such a polymer include phase conversion emulsification, acid deposition and forced emulsification.

[0078] One known example of the phase conversion emulsification comprises: dissolving a self-water-dispersible resin (self-water-dispersible polymer), in which a part of the acid group is neutralized with a base, in an organic solvent; dispersing or dissolving a pigment and/or dye in the resulting solution to give a colorant resin solution; and mixing it with an aqueous medium essentially comprising water, to thereby undergo phase conversion emulsification. Upon the phase conversion emulsification, colorant particles in which the pigment and/or dye is enveloped in the resin are generated. Therefore, by subsequently removing the organic solvent from the aqueous medium, a colorant enveloping the pigment and/or dye can be suitably obtained. Preferred examples of the self-water-dispersible resin include copolymers of at least one monomer selected from the group consisting of styrene, substituted styrenes and (meth)acrylates, having an acid value of from 20 to 200 KOH mg/g, with (meth)acrylic acid.

[0079] Another known example of the phase conversion emulsification comprises adding a polyester to a ketone solvent together with the pigment and/or dye, adding a neutralizing agent to the ketone solution to thereby ionize the carboxyl group in the polyester, and adding water thereto to undergo phase conversion emulsification. By evaporating away the ketone solvent from the mixed solvent, and a colorant enveloping the pigment and/or dye in a polyester can be suitably obtained.

[0080] One example of the acid deposition process comprises adding an acidic compound to an aqueous dispersion of the pigment and/or dye finely dispersed by a "resin (polymer) having a carboxyl group neutralized with a basic compound" to make the pH of the aqueous dispersion neutral or acidic, thereby making the resin hydrophobic so that the pigment can be firmly fixed onto the resin. By subsequently adding a basic compound to the aqueous dispersion so as to neutralize again the carboxyl group in the resin, an aqueous dispersion of a colorant enveloping the pigment and/or dye in a resin (polymer) can be suitably obtained.

[0081] One known example of the forced emulsification process comprises adding a vinyl polymer having a silicon macromer as a copolymerizable component, and the pigment and/or dye to an organic solvent, adding a neutralizing agent to the resulting solution or dispersion to thereby ionize the salt-forming group in the vinyl polymer, and adding water thereto to emulsify it. By subsequently evaporating away the organic solvent, a colorant enveloping the pigment and/or dye in the polymer can be suitably obtained.

[0082] The polymer that envelops pigment and/or dye therein is typically a copolymer of a polymerizable group-having dispersant and a copolymerizable monomer, which will be described in detail below. The colorant of the pigment and/or dye enveloped in such a copolymer of a polymerizable group-having dispersant and a copolymerizable monomer can be suitably obtained by dispersing the pigment and/or dye in water by a polymerizable group-having dispersant, followed by adding a copolymerizable monomer and a polymerization initiator thereto to undergo polymerization.

[0083] It is preferred that the particles in the ink jet recording ink have a relatively uniform particle size from the views

sion at 60°C under reduced pressure, and a crosslinking reaction was carried out at 80°C for 5 hours. Next, the pH thereof was controlled to around 8 with potassium hydroxide, and this was filtered through a 0.4 μm filter to obtain an intended colorant dispersion. The mean particle size thereof was measured with a Doppler-laser particle size distribution analyzer, Microtrac UPA 150 manufactured by Leeds & Northrup, and found to be 180 nm. The solid content was 34 %.

<Preparation of pigment having polymer group bonded to its surface>

(Colorant 6-1: black pigment)

[0260] An intended pigment having a polymer group bonded to its surface was prepared according to the method described in Example III and Example IV in WO995169 and Japanese Patent Laid-Open No. 95987/2000. The details thereof are described below.

[0261] 11.4 g of sodium nitrite, 28.0 g of sulfanilic acid and 1200 g of 0°C water were fed into a reactor to form diazonium sulfanilate, to which was added 200 g of a carbon black pigment, Raven C. When the generation of nitrogen ceased, the reaction mixture was concentrated, and further reacted at an elevated temperature. The resulting mixture was extracted with ethanol for 12 hours in a Soxhiet's extractor to remove unreacted compounds and side products, and this was again dissolved in water and filtered to obtain a dispersion of about 20 wt.% sulfanilate-processed carbon black pigment. On the other hand, 3.6 g of aminostyrene, 2.1 g of sodium nitrite and 150 g of water were fed into a separate reactor to form a diazonium salt of 4-aminostyrene, and this was dissolved in 10 g of ethanol. The sulfanilate-processed carbon black pigment dispersion was added to the diazonium salt solution and reacted for 18 hours with stirring. Then, this was filtered and purified through Soxhlet extraction to obtain a dispersion of a carbon black pigment having 4-aminostyrene added to its surface. Next, 30 g of deionized water was degassed in a nitrogen atmosphere at 90°C in a reactor, and a mixture of 28.13 g of the 4-aminostyrene-added carbon black pigment dispersion, 2.0 g of methyl methacrylate, 2.0 g of butyl acrylate, and 1.0 g of polyethylene glycol 2000 monomethyl ether acrylate dissolved in 3.0 g of deionized water was dropwise added thereto over a period of 20 minutes. 0.22 g of potassium persulfate was added thereto and reacted at 80°C for 18 hours. The resulting product was concentrated under reduced pressure, and extracted with acetone in an Soxhlet's extractor to remove the non-added polymer. The process gave an intended dispersion of a pigment having a polymer group bonded to its surface.

<Preparation of Inks>

[0262] Inks having the composition set forth below (see Table 1 to Table 32) were produced according to the following process. An aqueous medium prepared beforehand was gradually and dropwise added to the above-obtained dispersion of the colorant with stirring. After the dropwise addition, this was fully stirred, and filtered through a 5 μm membrane filter to obtain an ink.

[0263] In Table 1 below, "Ex. 1" indicates the ink of Example 1; and "Comp. 1" indicates the ink of Comparative Example 1. The same shall apply to the other example numbers in Table 1 and also to the example numbers in the other Tables.

[0264] In Tables 1 to 32 below, the numerals relating to the compositions of the inks indicate the contents of the respective constituent components in terms of % by weight with respect to the whole amount of each ink composition. The colorant is added in the form of a dispersion. Accordingly, the amount of the colorant dispersion added is calculated from the colorant content in the ink and from the solid concentration of the colorant dispersion.

[0265] Olfin E1010 (manufactured by Nisshin Chemical Industry), Olfin STG (manufactured by Nisshin Chemical Industry), and Surfynol 465 (manufactured by Air Product) are acetylene glycol surfactants. Surfynol 61 (manufactured by Air Product) is an acetylene alcohol surfactant.

[0266] The surface tension in Tables 1 to 31 below was measured with an automatic surface tension balance, Model CBVP-Z manufactured by Kyowa Kaimen Gagaku.

[0267] The inks of the Examples all have ΔSP of at least 1.0 cal/cm^3.

[0268] Regarding the colorants, the compounds of formula (1) and the compounds of formula (2), the numeral in the upper row indicates the content thereof, and the code in the lower row indicates the kind of the colorant, the compound of formula (1) or the compound of formula (2).

[0269] Specifically, the codes of the compounds shown in the Tables are as follows:

[1-1]: compound of formula (1), wherein R is neopentyl group, n is 1.0, m is 1.5, and M is hydrogen atom.
[1-2]: compound of formula (1), wherein R is t-butyl group, n is 1.0, m is 2.0, and M is hydrogen atom.
[1-3]: compound of formula (1), wherein R is 1,3-dimethylbutyl group, n is 0, m is 4.5, and M is hydrogen atom.
[1-4]: compound of formula (1), wherein R is isobutyl group, n is 3.0, m is 1.0, and M is hydrogen atom.

[2-4]: compound of formula (2), wherein n is 1.5, and EP is ethyleneoxy alone.
[2-5]: compound of formula (2), wherein n is 2.8, and EP is ethyleneoxy alone.
[2-6]: compound of formula (2), wherein n is 3.5, and EP is ethyleneoxy alone.
[2-7]: compound of formula (2), wherein n is 10, and EP is ethyleneoxy alone.
[2-8]: compound of formula (2), wherein n is 4.5, and EP is ethyleneoxy alone.
[2-9]: compound of formula (2), wherein n is 4, and EP is ethyleneoxy alone.
[2-10]: compound of formula (2), wherein n is 5, and EP is ethyleneoxy and propyleneoxy in a ratio of 3:1.
[2-11]: compound of formula (2), wherein n is 3, and EP is ethyleneoxy alone.

Table 1

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
colorant	7.5	4.5	5.5	5.0	7.5	4.5	5.5	5.0
	1-1	1-2	1-3	1-4	1-1	1-2	1-3	1-4
Olfin E1010	1.0						0.5	
Olfin STG			1.0					0.7
Surfynol 465		1.2						
Surfynol 61				0.5	1.0	1.0	0.5	0.3
DEGmBE	5.0				5.0			
TEGmBE		10.0		5.0			4.0	
PGmBE							1.0	
1,2-pentanediol				2.0				
1,2-hexanediol		3.0	5.0	3.0		5.0		5.0
1,6-hexanediol			5.0					
glycerin	14.0	9.0	9.0	14.0	14.0	9.0	12.0	12.0
diethylene glycol		5.0	7.0			5.0		
thiodiglycol			3.5				3.5	
trimethylolpropane								1.0
1,3-dimethyl-2-imidazolidinone				2.0	2.0	2.0	2.0	2.0
triethanolamine	0.8	0.9	1.0	0.7			0.9	0.9
potassium hydroxide			0.1		0.1	0.1		
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	34	32	34	34	35	33	32	32

Table 2

	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex.16
Colorant	7.0	7.0	7.5	4.5	5.5	7.5	7.5	5.5
	1-1	1-1	1-1	1-2	1-3	1-1	1-1	1-1
Olfin E1010			1.0			1.0		
Olfin STG		1.0			1.0			

Table 2 (continued)

	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex.16
Surfynol 465	0.5			1.2				
Surfynol 61	0.6							
DEGmBE	4.0			2.5	7.0			
TEGmBE			5.0				8.0	
PGmBE		2.0						
DPGmBE	1.0				3.0			
1,2-hexanediol	3.0	7.0	5.0	4.5	1.0			5.0
1,6-hexanediol					5.0			
Glycerin	10.0	10.0	12.0	10.0	10.0	12.0	12.0	12.0
diethylene glycol		2.0			7.0			
tetraethylene glycol				5.0				
Thiodiglycol		3.0			3.5			
1,3-dimethyl-2-imidazolidinone	2.0							
Triethanolamine	0.9		0.8	0.9	0.9	0.8	0.8	0.8
potassium hydroxide		0.1						
Proxel XL-2	0.03	0.03	0.03	0.03	003	0.03	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	30	32	33	33	32	33	35	34

Table 3

	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24
Colorant	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
	1-1	1-1	1-1	1-1	1-1	1-1	1-1	1-5
Olfin E1010						1.0		1.0
Surfynol 61	0.5					0.5		
DEGmBE		8.0						5.0
TEGmBE				5.0			3.0	
PGmBE				1.0				
1,2-pentanediol			4.0		2.0			
1,2-hexanediol					3.0		5.0	
Glycerin	12.0	12.0	12.0	12.0	12.0	12.0	12.0	14.0
1,3-dimethyl-2-imidazolidinone	2.0			2.0		1.0		
Triethanolamine	0.8	0.8	0.8	0.8	0.8			0.8
potassium hydroxide						0.10	0.10	

Table 3 (continued)

	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	35	35	34	36	34	31	36	34

Table 4

	Ex. 25	Ex. 26	Ex. 27	Ex. 28	Ex. 29	Ex. 30	Ex. 31	Ex. 32
Colorant	4.5	5.5	5.0	7.5	4.5	5.5	3.0	5.0
	1-6	1-7	1-8	1-20	1-20	1-20	3-1	3-2
Olfin E1010			0.5	1.0				1.0
Olfin STG		1.0				0.5	1.0	
Surfynol 465	1.2				1.2			
Surfynol 61			0.5					
DEGmBE				5.0			7.0	
TEGmBE	10.0		5.0		10.0			6.0
PGmBE							2.0	
1,2-pentanediol			2.0					
1,2-hexanediol	3.0	5.0	3.0			1.0		2.0
1,6-hexanediol		5.0				5.0		
Glycerin	9.0	9.0	14.0	10.0	9.0	9.0	14.0	15.0
diethylene glycol	5.0	7.0			5.0	7.0		
tetraethylene glycol						3.5		
Thiodiglycol		3.5						
1,3-dimethyl-2-imidazolidinone			2.0			2.0		
Triethanolamine	0.9	1.0	0.7	0.8	0.9	0.8		0.9
potassium hydroxide		0.1					0.1	
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	003	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	32	34	31	33	32	32	32	34

Table 5

	Ex. 33	Ex. 34	Ex. 35	Ex. 36
Colorant	5.0	5.5	5.0	5.5
	3-3	3-4	3-4	3-4

Table 5 (continued)

	Ex. 33	Ex. 34	Ex. 35	Ex. 36
Olfin E1010			1.0	
Surfynol 465	1.0			
Surfynol 61	0.5	1.0		
DEGmBE	8.0	8.0		
TEGmBE				4.0
PGmBE		2.0		
1,2-hexanediol			5.0	5.0
Glycerin	15.0	7.0	15.0	15.0
diethylene glycol		5.0		
tetrapropylene glycol		5.0		
Trimethylolpropane	1.0			1.0
1,3-dimethyl-2-imidazolidinone		2.0		
Triethanolamine	0.5	0.9	0.9	0.3
potassium hydroxide	0.05	0.1		0.1
Proxel XL-2	0.03	0.03	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance
surface tension (mN/m)	31	28	34	31

Table 6

	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 43	Ex. 43	Ex. 44
Colorant	4.0	3.0	4.0	3.0	4.0	3.0	4.0	3.0
	4-1	4-2	4-1	4-2	4-1	4-2	4-1	4-2
Olfin E1010	1.0						0.5	
Olfin STG			1.0					0.7
Surfynol 465		1.2						
Surfynol 61				0.5	1.0	1.0	0.5	0.3
DEGmBE	5.0				5.0			
TEGmBE		10.0		5.0			4.0	
PGmBE							1.0	
DPGmBE								
1,2-pentanediol				2.0				
1,2-hexanediol		3.0	5.0	3.0		5.0		5.0
1,6-hexanediol			5.0					
Glycerin	14.0	9.0	9.0	14.0	14.0	9.0	12.0	12.0
diethylene glycol		5.0	7.0			5.0		
tetraethylene glycol								
thiodiglycol			3.5				3.5	

Table 6 (continued)

	Ex. 37	Ex. 38	Ex. 39	Ex. 40	Ex. 41	Ex. 43	Ex. 43	Ex. 44
trimethylolpropane								1.0
1,3-dimethyl-2-imidazolidinone				2.0	2.0	2.0	2.0	2.0
triethanolamine	0.8	0.9	1.0	0.7			0.9	0.9
potassium hydroxide			0.1		0.1	0.1		
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	34	32	34	34	35	33	32	32

Table 7

	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49	Ex. 50	Ex. 51	Ex. 52
Colorant	4.0	3.0	4.0	3.0	4.0	3.0	4.0	3.0
	4-1	4-2	4-1	4-2	4-1	4-2	4-1	4-2
Olfin E1010			1.0					
Olfin STG		1.0						
Surfynol 465	0.5							
Surfynol 61	0.5					0.5		0.3
DEGmBE	4.0						8.0	
TEGmBE				8.0				
PGmBE		2.0						
DPGmBE	1.0							
1,2-pentanediol								4.0
1,2-hexanediol	3.0	7.0			5.0			
1,6-hexanediol								
Glycerin	10.0	10.0	12.0	12.0	12.0	12.0	12.0	12.0
diethylene glycol		2.0						
thiodiglycol		3.0						
1,3-dimethyl-2-imidazolidinone	2.0					2.0		
triethanolamine	0.9		0.8	0.8	0.8	0.8	0.8	0.8
potassium hydroxide		0.1						
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	30	32	33	35	34	35	35	34

Table 9 (continued)

	Ex. 57	Ex. 58	Ex. 59	Ex. 60	Ex. 61	Ex. 62	Ex. 63	Ex. 64
Isomalto-oligosaccharide			2.0					
Sorbitol				3.0				
Fructose					3.0			
Xylitol						5.0		
Glucose							3.0	
Xylose								5.0
diethylene glycol			7.0				5.0	
thiodiglycol			3.5	3.5				3.5
1,3-dimethyl-2-imidazolidinone					2.0	2.0	2.0	2.0
triethanolamine	0.8	0.9	1.0	1.0	0.7			0.9
potassium hydroxide			0.1	0.1		0.1	0.10	
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	34	34	31	35	35	36	34	33

Table 10

	Ex. 65	Ex. 66	Ex. 67	Ex. 68	Ex. 69	Ex. 70	Ex. 71	Ex. 72
Colorant	5.0	7.0	7.0	7.5	7.5	7.5	7.5	7.5
	1-4	1-1	1-1	1-1	1-1	1-1	1-1	1-1
Olfin E1010				1.0				
Olfin STG	0.7		1.0					
Surfynol 465		0.5						
Surfynol 61	0.3	0.5					0.5	
DEGmBE		4.0						8.0
TEGmBE					8.0			
PGmBE			2.0					
DPGmBE		1.0						
1,2-hexanediol	5.0	3.0	7.0			5.0		
Glycerin	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Maltitol	1.0	2.5		1.0		2.0		
Maltose				3.0			2.0	
Erythritol					2.0			
Mannitol	2.0						1.0	
Sorbitol			2.0		3.0			

Table 11 (continued)

	Ex. 73	Ex. 74	Ex. 75	Ex. 76	Ex. 77	Ex. 78	Ex. 79	Ex. 80
Xylose						2.0	1.0	
diethylene glycol							5.0	7.0
Thiodiglycol								3.5
1,3-dimethyl-2-imidazolidinone		2.0		1.0			2.0	
Triethanolamine	0.8	0.8	0.8			0.8	0.9	1.0
potassium hydroxide				0.10	0.10			0.1
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	35	37	35	32	37	35	33	35

Table 12

	Ex. 81	Ex. 82	Ex. 83	Ex. 84	Ex. 85	Ex. 86	Ex. 87
Colorant	5.0	3.0	5.0	5.0	5.5	5.0	5.0
	1-8	3-1	3-2	3-3	3-4	3-2	3-3
Olfin E1010	0.5		1.0			1.0	
Olfin STG		1.0					
Surfynol 465				1.0			
Surfynol 61	0.5			0.5	1.0		
DEGmBE		7.0		8.0	8.0		
TEGmBE	5.0		6.0				4.0
PGmBE		2.0			2.0		
1,2-pentanediol	2.0						
1,2-hexanediol	3.0		2.0			5.0	5.0
Glycerin	10.0	11.0	11.0	11.0	7.0	10.0	10.0
Maltitol	1.0		1.0		2.0		2.0
Maltose	1.0			2.0			
Erythritol	1.0					1.0	
isomalto-oligosaccharide			1.0			1.0	
Sorbitol		1.0		2.0		2.0	
Fructose			1.0				2.0
Xylitol		1.0			2.0		
Xylose		2.0					
diethylene glycol					5.0		
tetrapropylene glycol					5.0		
Trimethylolpropane				1.0			1.0

Table 13 (continued)

	Ex. 88	Ex. 89	Ex. 90	Ex. 91	Ex. 92	Ex. 93	Ex. 94	Ex. 95
Triethanolamine	0.8	0.9	1.0	0.7			0.9	0.9
potassium hydroxide			0.1		0.1	0.1		
Proxel XL-2	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Benzotriazole	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	balance	balance	balance	balance	balance	balance	balance	balance
surface tension (mN/m)	35	33	35	35	36	34	33	33

Table 14

	Ex. 96	Ex. 97	Ex. 98	Ex. 99	Ex. 100	Ex. 101	Ex. 102	Ex. 103
Colorant	4.0	3.0	4.0	3.0	4.0	3.0	4.0	3.0
	4-1	4-2	4-1	4-2	4-1	4-2	4-1	4-2
Olfin E1010			1.0					
Olfin STG		1.0						
Surfynol 465	0.5							
Surfynol 61	0.5					0.5		
DEGmBE	4.0						8.0	
TEGmBE				8.0				
PGmBE		2.0						
DPGmBE	1.0							
1,2-pentanediol								4.0
1,2-hexanediol	3.0	7.0			5.0			
1,6-hexanediol								
Glycerin	8.0	8.0	10.0	10.0	10.0	10.0	10.0	10.0
Maltitol	1.0	2.5		1.0		2.0		
Maltose				3.0			2.0	
Erythritol					2.0			
isomalto-oligosaccharide								
Mannitol	2.0						1.0	
Sorbitol			2.0		3.0			
Fructose						2.0		
Xylitol		2.5		1.0				
Glucose								
Xylose			3.0					4.0
diethylene glycol								
Thioglycol		3.0						
Trimethylolpropane								